JOAP-TSC-TR-0202

EFFECT OF USING VHG METALLO-ORGANIC CONCENTRATES IN PRODUCTION OF JOAP SPECTROMETRIC STANDARDS

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This report has been reviewed by the undersigned and is approved for publication in accordance with the Joint Regulation and JOAP-TSC charter.

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14. ABSTRACT

The previous sole source supplier of metallo-organic concentrates used in the production of JOAP calibration/standardization fluids made a business decision to discontinue the sale of its concentrates. This decision was a signal to the Joint Oil Analysis Program Technical Support Center (JOAP-TSC) to begin the search for and qualification of new suppliers of concentrates. The JOAP-TSC tested the effects from using VHG Labs, Inc. metallo-organic concentrates in the preparation of JOAP spectrometric standards. The new VHG-based standards were blended and QC tested according to normal JOAP-TSC production methods. Once accepted, the standards would be further tested for their effects on the Joint program in used oil sample testing. Used oil tests were performed to show the comparability of results obtained on spectrometers calibrated/standardized with either VHG or Conostan blends. The purpose of the tests was to ensure that the limits in the JOAP Manual Volume 3 would not change. Testing demonstrated that the JOAP blends prepared from the concentrates manufactured by VHG Labs, Inc. met the requirements of the JOAP and are interchangeable with current JOAP standards.

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EFFECT OF USING VHG METALLO-ORGANIC CONCENTRATES IN PRODUCTION OF JOAP SPECTROMETRIC STANDARDS

I. EXECUTIVE SUMMARY:

Since the mid 1970's JOAP spectrometric reference materials (standards) have been blended from commercially supplied metallo-organic concentrates of specific Alkyl Aryl Sulfonate composition. At present the Joint Oil Analysis Program Technical Support Center (JOAP-TSC) produces these JOAP reference materials used in the calibration and routine standardization of all JOAP atomic emission spectrometers (AES).

The previous sole source supplier of metallo-organic concentrates made a business decision to discontinue the sale of its concentrates. This decision was a signal to the Joint Oil Analysis Program Technical Support Center (JOAP-TSC) to begin the search for and qualification of new suppliers of concentrates. The JOAP-TSC tested the effects from using VHG Labs, Inc. metallo-organic concentrates in the preparation of JOAP spectrometric standards. The new VHG-based standards were blended and QC tested according to normal JOAP-TSC production methods. Once accepted, the standards would be further tested for their effects on the Joint program in used oil sample testing.

Used oil tests were performed to show the comparability of results obtained on spectrometers calibrated/standardized with either VHG or Conostan blends. The purpose of the tests was to ensure that the limits in the JOAP Manual Volume 3 would not change.

Testing demonstrated that the JOAP blends prepared from the concentrates manufactured by VHG Labs, Inc. met the requirements of the JOAP and are interchangeable with current JOAP standards.

The original VHG 19 blends have met the JOAP criteria during their first round of shelf life testing. Shelf life testing on the standards blended from the VHG concentrates is ongoing and will continue until degradation of the blends is observed or 30 months has passed, whichever comes first.

II. INTRODUCTION:

A. Purpose:

To identify and qualify a new supplier for the metallo-organic concentrates used in the production of the JOAP standard reference materials.

B. Background:

The JOAP-TSC manufactures spectrometric oil standards used for the calibration of DoD atomic emission spectrometers and for daily standardization of these instruments in field

laboratories. The atomic emission spectrometers are used in the determination of wear metals and additives in lubricants drawn from various JOAP-member land, air, sea and support equipment. Routine analysis of JOAP equipment provides valuable information to engine and equipment managers who use this information in whole or part as a basis for maintenance decisions.

In the past, all of the single element metallo-organic concentrates that were used in the JOAP standards production were purchased from CONOSTAN, a sole source supplier. CONOSTAN elected to discontinue selling the concentrates to outside organizations. In response to this decision, the JOAP-TSC identified other manufacturers of metallo-organic concentrates and performed screening tests on the concentrates of two of the manufacturers—VHG Labs, Inc. and Alfa Aesar. In depth testing was performed using the metallo-organic concentrates manufactured by VHG Labs, Inc. based on the fact that the blends from the VHG concentrates had fewer failures during the screening tests and the restrictive time constraints on locating a new supplier for the metallo-organic concentrates.

C. Participants:

JOAP-TSC staff
Dr. Dave Sherry, University of West Florida
Captain Steinfadt, AFOAP
Dan McElroy, AOAP
Elizabeth Ann Lurton, NOAP

III. TEST OBJECTIVES and METHODS:

A. Objective 1. Research the compatibility of the concentrates.

Method.

1. Review concentrate literature from VHG and report on differences between VHG and current supplier, CONOSTAN.

B. Objective 2. Evaluate blending and solubility of VHG concentrates.

Method.

1. Blend a combined 19 element (D19) reference standard using VHG concentrates, MIL-L-6082 base oil and VHG amine sulfonate stabilizer. Blend standards in concentrations of 5 PPM, 10 PPM, 30 PPM, 50 PPM, and 100 PPM. Document any differences in consistency of concentrates; difficulties blending, time to blend and solubility of concentrates. Evaluate the amount of rotation/mixing time that is required for the VHG standards to obtain a homogeneous sample. Visually examine for precipitates and/or separation after dissolution of concentrates. A second chemist will duplicate III.B.1.

2. After the standards in III.B.1 have passed visual testing, blend D19 reference standards using VHG concentrates at concentrations of 300 PPM, 500 PPM, 700 PPM, and 900 PPM. Visually examine for precipitates or separation after dissolution of concentrates. Document any differences in consistency of concentrates; difficulties blending, time to blend and solubility of concentrates. Evaluate the amount of rotation/mixing time that is required for the VHG standards to obtain a homogeneous sample. Visually examine for precipitates and/or separation after dissolution of concentrates. A second chemist will duplicate III.B.2.

3. Blend the twelve element (D12) standard using VHG concentrates, MIL-L-6082 base oil and VHG amine sulfonate stabilizer at the following concentrations: 5 PPM, 10 PPM, 30 PPM, 50 PPM, 100 PPM, 300 PPM and 900 PPM. Document any differences in consistency of concentrates; difficulties blending, time to blend and solubility of concentrates. Evaluate the amount of rotation/mixing time that is required for the VHG standards to obtain a homogeneous sample. Visually examine for precipitates and/or separation after dissolution of concentrates. A second chemist will duplicate III.B. 3.

C. Objective 3. Evaluate the response of JOAP certified spectrometers to standards blended from the concentrates.

Method.

1. Using a JOAP approved spectrometer, analyze the VHG standards from III.B.1 and III.B.2 against their JOAP D19 counterparts blended from Conostan concentrates of the same concentration; statistically compare the results.

   a. The spectrometer is to be standardized according to manufacturer's instructions and with JOAP standards. It is calibrated with JOAP standards made from Conostan concentrates. The results are statistically analyzed and compared using mean, mean difference, standard deviation, t-test, and F test.

   b. If the VHG standards do not pass JOAP QA, determine whether the VHG standards can be adjusted to meet established minimum JOAP-TSC QA limits for standards. A maximum of three adjustments are allowed before classifying the standard as failing.

   c. If the VHG 19 element standards pass JOAP QA with or without adjustment, re-standardize the spectrometer with the 19 element standards blended from VHG concentrates and analyze the 12 element and 3 element standards blended from VHG concentrates at concentrations of 5 PPM, 10 PPM, 30 PPM, 50 PPM, and 100 PPM, III.B.3, against their 19 element VHG counterparts.

   d. If 12 element and 3 element VGH standards meet QA requirements, perform daily checks of JOAP and VHG 12 and 3 element standards on a spectrometer standardized with VHG 12 and 3 element standards. **Limits for standardization**

are found in the Operation and User Manual, Spectroil M Oil Analysis Spectrometers, page 4-14, Table 4-1.

Procedure.

i.) Standardize a Spectroil M spectrometer with 12 and 3 element standards blended with VHG concentrates.

ii.) Perform 5 analyses of the 12 element 100 PPM VHG standard. Average results and compare to limits.

iii.) Perform 5 analyses of the 3 element 100 PPM VHG standard. Average results and compare to limits.

iv.) Perform 5 analyses for each concentration of JOAP D12 and D3 standard. Average results.

v.) Perform 5 analyses for each concentration of 12 element and 3 element standards blended from VHG concentrates. Average results.

vi.) Compare averages to established limits.

D. Objective 4. Evaluate the impact of new concentrates on analysis of "used" oil samples.

Method.

1. Analyze field samples on a JOAP approved spectrometer calibrated with JOAP reference standards prepared from Conostan concentrates and standardized with JOAP D12/D3 standards prepared from CONOSTAN concentrates. Calibrate a JOAP approved spectrometer with D19 standards prepared from VHG concentrates; standardize the spectrometer with D12/D3 standards prepared from VHG concentrates; and analyze the same field samples that were analyzed on the JOAP calibrated/JOAP standardized spectrometer. Determine if a systematic bias occurs because of using VHG concentrates in blending JOAP standards. If a bias does occur, determine if JOAP wear-metal limits and guidelines are affected by the bias.

E. Objective 5. Evaluate the stability of and a viable shelf life for the standards blended from VHG concentrates.

Shelf life Method Analyze the standards made from each manufacturer's concentrates at three-month intervals for up to 30 months to determine the shelf life of the blend.

1. Standardize a JOAP approved spectrometer.

2. Perform 5 spectrometric analyses of a JOAP D19 reference standard prepared from Conostan concentrates whose concentration is the same as the candidate to be tested.

3. Determine the average values for the 5 analyses of the D19 reference standard.

4. Perform 5 spectrometric analyses of the candidate.

5. Determine the average values for the 5 analyses of the candidate.

6. Compare the results to established limits for JOAP standards.

IV. TEST EXECUTION:

A. Test Environment: All tests for objectives 1 through 4 were conducted at the JOAP-TSC including the JOAP laboratory located within the JOAP-TSC. Tests for objective 5 are ongoing and conducted at the JOAP-TSC.

B. Operational Support:

1. Oversight for statistical analysis of data gathered during this test was provided by Dr. Dave Sherry, Department of Statistics and Mathematics, University of West Florida.

V. TEST DATA, RESULTS and DISCUSSION:

A. Objective 1. Research the compatibility of the concentrates.

The JOAP-TSC obtained and compared material safety data sheets from VHG Labs, Inc and CONOSTAN for each of the 19 elements that are used in the production of the JOAP standards. The comparison was performed to determine the differences, if any, in the chemistries used by the two manufacturers.

Eighteen of the nineteen concentrates produced by CONOSTAN are metal alkylaryl sulfonates; the silicon concentrate is a silicone fluid. Each of the 19 concentrates contains white mineral oil, or solvent neutral oil or both in the composition of the concentrate.

Eleven of the nineteen concentrates produced by VHG Labs, Inc. are metal alkylaryl sulfonates; six of the concentrates are carboxylates; titanium is a phenolate; silicon is a silicone fluid. The alkylaryl sulfonates and the silicon concentrate contain white mineral oil, or solvent neutral or ~~a~~ both in the composition of the concentrate. The carboxylates are dissolved in mineral spirits.

Because four chemistries are used in the VHG concentrates that are not used in the JOAP standards, it was important to determine if side effects occur from mixing the chemistries, if there are special requirements for handling the different chemistries, etc.

B. Objective 2. Evaluate blending and solubility of VHG concentrates.

1. Gary Humphrey, a JOAP-TSC chemist, used VHG concentrates to blend 19 element standards at the following concentrations: 5PPM, 10PPM, 30PPM, 50PPM, and 100PPM. During the blending process, it became apparent that several of the concentrates were too viscous, making it difficult to obtain accurate measurements during the weighing process. The blends were rotated for 24 hours and allowed to stand 4 hours before they were visually checked. The blends did not appear homogeneous; separate constituents could be seen clinging to the plastic container. VHG Labs was contacted and asked to decrease the viscosities of those particular concentrate blends. VHG Labs blended new concentrates and these concentrates were used for all phases of the test. The VHG metal concentrates whose viscosities required adjustment were silver, aluminum, molybdenum, magnesium and vanadium. Marilyn Squalls, a JOAP-TSC chemist, duplicated the process of blending the different concentrations using the new VHG concentrates. Marilyn Squalls did not experience any difficulty with obtaining accurate weighing results. Each concentration was rotated for 24 hours and visually checked. The blends appeared to be homogeneous and no separation of concentrates was observed.

2. Gary Humphrey used VHG concentrates to blend 19 element standards at the following concentrations: 300PPM, 500PPM, 700PPM, and 900PPM. The blends were rotated for 24 hours and visually checked. The blends appeared to be homogeneous and showed no separation of concentrates. Marilyn Squalls duplicated the process of blending the different concentrations using the VHG concentrates. Each concentration was rotated for 24 hours and allowed to stand 4 hours before they were visually checked. The blends appeared to be homogeneous and no separation of concentrates was observed. Neither chemist experienced any difficulty with obtaining accurate measurements during the weighing process.

3. Marilyn Squalls used VHG concentrates to blend 12 element standards at the following concentrations: 5 PPM, 10PPM, 30PPM, 50PPM, 100PPM, 300PPM and 900PPM. A three element standard was blended at 100PPM concentration. The 5PPM, 10PPM, 30PPM, 50PPM and 100PPM concentrations and the three element blend were rotated for 3 hours; the mixtures were visually checked and appeared to be homogeneous. The 300PPM and 900PPM blends were rotated for 24 hours and visually checked. The blends were homogeneous and showed no separation of concentrates. Vee Bersabal, a JOAP-TSC chemist, duplicated the process of blending the different concentrations using the VHG concentrates and using the same rotation times. The blends were visually checked and appeared to be homogeneous with no separation of concentrates being observed.

C. Objective 3. Evaluate the response of JOAP certified spectrometers to standards blended from the concentrates.

1. Quality assurance testing personnel at the JOAP-TSC used a JOAP certified Spectroil M/N spectrometer, S/N 0794, to perform the quality assurance testing.[1] The spectrometer was standardized with JOAP standards and the 19 element blends from VHG concentrates, III.B.1. and III.B.2.,were tested against their JOAP D19 counterparts and the results were statistically compared.[2] The following statistics were used to compare the VHG blend to its JOAP counterpart: mean, mean difference, standard deviation, F test, the student t-test and the practical tolerance test. The F test is employed only if the reference or candidate standard exceeds the standard deviation limit. The practical tolerance test was developed for the JOAP by the Naval Post Graduate School to test t-test failures. If a t-test failure occurred because the candidate's standard deviation was much smaller than that of the JOAP reference, then the failure was not counted against the candidate. A VHG blend was allowed a maximum of three adjustments in order to meet the mean difference requirements before it was deemed as failing the quality assurance testing. Blends with concentrations above 100 PPM were tested at 100 PPM concentration level by diluting a small quantity to 100 PPM and testing that dilution. Plus/minus 9% was used for the mean difference requirement for 500PPM, 700PPM and 900PPM; plus/minus 9% is based upon the Operation and User Manual, Spectroil M Oil Analysis Spectrometers, Table 4-3, page 4-32.

   After quality assurance demonstrated that the VHG 19 element blends met the JOAP criteria, JOAP-TSC personnel performed quality assurance testing on the VHG 12 element blends. The 12 element blends were tested against the VHG 19 element blends of the same concentration. The Spectroil M/N spectrometer was standardized with the VHG 19 element blends. The procedures and limits used in the testing are the same as those used for testing the VHG 19 element blends.

   The original set of VHG 19 element blends blended from the VHG concentrates met the JOAP requirements. The signed, original data and statistical analyses are on file at the JOAP-TSC.

   The duplicate set of VHG 19 element blends met the requirements for JOAP. The signed, original data and statistical analyses are on file at the JOAP-TSC.

   The original set of VHG 12 element blends and the 3 element blend met the requirements for JOAP. The signed, original data and statistical analyses are on file at the JOAP-TSC.

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[1] Quality assurance testing is performed by Marilyn Squalls and Vee Bersabal, chemists, and Michael Poff, materials engineering technician and Sharon Hem, physical science technicians.

[2] Gary Humphrey, Marilyn Squalls, Allison Toms, Timothy Yarborough, and Vee Bersabal, chemists, reviewed the data and statistics as well as James R. Holland, Technical Director, Michael Poff, , materials engineering technician, and Dr. David L. Sherry, PhD., University of West Florida Math Department Chairman.

The duplicate set of VHG 12 element blends and the 3 element blend met the requirements for JOAP. The signed, original data and statistical analyses are on file at the JOAP-TSC.

2. Whatever the concentrates used in the JOAP standards, it should be transparent to the customer. It is plausible that a customer would be in possession of JOAP standards that were blended from both CONOSTAN concentrates and VHG concentrates. To demonstrate the interchangeability of blends made with concentrates from both manufacturers, the Spectroil M spectrometers, S/N 0794 and S/N 0620, were standardized with VHG 12 and 3 element blends and check burns were performed on each VHG 12 and 3 element blend and on their JOAP counterparts. Each blend was analyzed 5 times and the analyses were averaged. All of the standards, regardless of what concentrates were used to produce them, when analyzed, were within the limits established for the JOAP standards (**Limits for standardization are found in the Operation and User Manual, Spectroil M Oil Analysis Spectrometers, page4-14, Table 4-1.**).

D. **Objective 4. Evaluate the impact of new concentrates on analysis of "used" oil samples.**

1. Data generated in this objective from samples analyzed using the JOAP-TSC Atomic Emission Spectrometer 0794 is found to be unusable. The data from the Conostan/JOAP calibration curves with Conostan/JOAP standardization (CC) and also data from the Conostan/JOAP calibration curves with VHG standardization (CV) were based on an incorrect Conostan/JOAP calibration curve in the spectrometer. The significance of this is that of the four sample sub-classes (CC, CV, VC, and VV) the CC is the control class. Therefore since the remaining classes do not correlate to the control it was decided that the data will be excluded from data analyses and will not be commented on in the conclusion. Only the data from the twenty samples analyzed using the JOAP-TSC Atomic Emission Spectrometer 0620 are used. Spectrometer 0620 had an accurate calibration curve.

2. The pass/fail criteria are based on the accuracy index, AI. An accuracy index is calculated as the difference in means (of the ten burns for each sub-class CV, VC and VC) and the control, CC (for the 20 samples); there are three AI values per sample. The AI for each element and each standard must be less than or equal to the accepted AI values in Table 1.

3. Note that the AI values listed here are derived for reference standards specifically but used as benchmarks in this test. It is reasonable to assume that any otherwise derived accuracy limits for this test would not be lower.

4. There were no failures in this objective thus the test did not indicate an adverse impact on the analysis of used JOAP samples by using JOAP standards blended from

VHG concentrates. The data collected is on file with the JOAP-TSC and available upon request.

5. The accuracy index is calculated as follows:

$$AI = abs(\bar{X} - \bar{Y})$$

where,

$\bar{Y}$ = **Average value of 10 consecutive burns for CV, VC and VV**
$\bar{X}$ = **Average value of 10 consecutive burns for CC**

ACCURACY INDICES

Concentration PPM	Elements: Al, Cr, Ni Si	Ti, B	Pb, Sn	Fe, Ag, Mo	Cu, Mg	Zn	Na
0	0.88	0.89	1.60	0.91	0.92	0.96	1.01
5	1.20	1.30	1.98	1.50	1.61	1.99	2.59
10	1.59	1.78	2.43	2.21	2.44	3.19	4.36
30	3.33	3.93	4.47	5.23	5.91	8.15	11.60
50	5.12	6.14	6.64	8.29	9.43	13.10	18.90
100	9.65	11.70	12.20	16.00	18.20	25.60	37.10
300	27.80	33.90	34.30	46.70	53.50	75.60	110.00
500	46.00	56.10	56.60	77.50	88.80	126.00	183.00
700	64.20	78.30	78.80	108.00	124.00	176.00	255.00
900	82.40	101.00	101.00	139.00	159.00	226.00	328.00

Table 1

E. Objective 5. Evaluate the stability of and a viable shelf life for the standards that are blended from VHG concentrates.

1. The VHG 19, 12 and 3 element blends are tested at 6month intervals up to thirty months, the shelf life of the JOAP standards. Currently, the original set of VHG 19 element blends has undergone the first round of shelf life testing and has met the JOAP requirements. Original data are on file at the JOAP-TSC.

CONCLUSIONS:

1. The metallo-organic concentrates manufactured by VHG Labs, Inc. can be used in the blending of JOAP standards and are interchangeable with current JOAP standards.

2. Shelf-life testing on the VHG 19, 12 and 3 element blends must continue at least until the blends start to show significant degradation or for 30 months, whichever comes first. This testing is necessary for determining whether the JOAP must change the assigned shelf lives of the JOAP standards.

3. For objective 4 testing, there was a possibility of 900 pass/fail decisions (i.e., mean comparisons). The data shows that 219 comparisons were not possible due to a very likely absence of the element. Thus, 681 pass/fail decisions were made. All were passes.

OBSERVATIONS:

1. It was observed that the VHG blends with the VHG Boron concentrate are superior to Conostan blends using Conostan's Boron concentrate. There were no observations indicating VHG blends suffered with elemental Boron precipitation while this is a common problem with Conostan blends.